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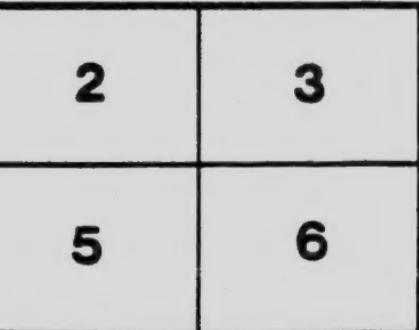
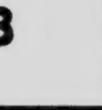
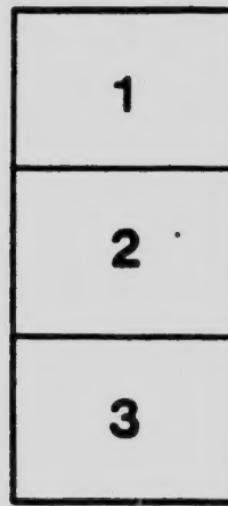
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UNIVERSITY OF TORONTO
STUDIES

PAPERS FROM THE PHYSICAL
LABORATORIES

No. 73: THE ABSORPTION OF GASES BY CARBONIZED
LIGNITES, BY STUART MCLEAN

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The Adsorption of Gases by Carbonized Lignites

By STUART MCLEAN, M.A.

Presented by PROF. E. F. BURTON, F.R.S.C.

(Read May Meeting, 1919.)

The term "adsorption" is applied to that property possessed by charcoals, lignites and other porous bodies of absorbing gases that are in contact with them. For charcoal, the phenomenon has been shown to consist of a condensation of the gas upon its surface, which takes place rapidly, requiring only a few minutes to reach the maximum, and a slow diffusion of the gas into the interior. Some authorities² claim that, in a few cases, they have found evidence that chemical action accompanies the process or that some of the gas is adsorbed permanently.

The object of the first series of experiments to be described below was to investigate the amount of gas adsorbed by a sample of carbonized lignite and how that amount varies with the pressure of the gas and the temperature of the lignite. A second series of experiments was undertaken to determine the nature of the process, especially to find out whether, or not, any chemical action or permanent adsorption takes place.

The lignites for these experiments were prepared by Mr. E. Stansfield of the Department of Mines, Ottawa, Ontario. Their densities were found by the volumenometer method³, the apparatus being filled with helium because that gas is not adsorbed at ordinary temperatures. Before each experiment the samples of lignite were heated to a temperature sufficient to free them from any previously absorbed gas and while hot, the apparatus containing them was exhausted.

A diagram of the apparatus used in the first experiments is shown in Fig. 1. The lignite is contained in the tube X which may be shut off from the rest of the apparatus at B. The gas used was measured in the graduated tube K and admitted at E. The mercury reservoir N was so arranged that it could be easily raised, thereby forcing all the gas in the tube K into the apparatus. The stop-cock B was then

¹ McBain, Phil. Mag. 18, 1909. Pa. 916.

² Arrhenius: Theories of Solutions.

Rhead and Wheeler, J. Chem. Soc. 103, 1913. Page 641.

³ McLean: Proc. Roy. Soc. of Canada. 1919.

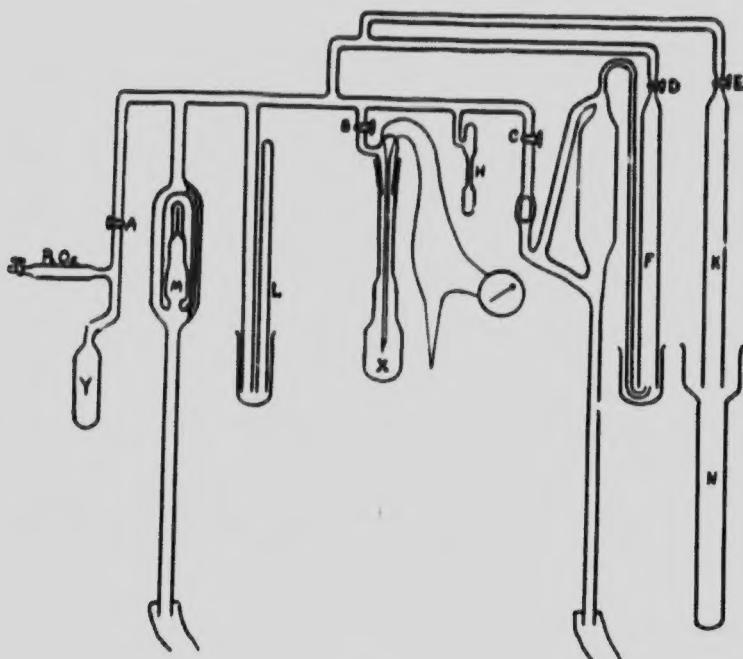


Figure 1

turned and the lignite exposed to the gas until the pressure, read on the manometer L, became constant. Since its density had been determined, the volume of the lignite in the tube X could be calculated. Subtracting this from the volume of the empty apparatus, which had been previously determined, the volume of the unadsorbed gas in the apparatus is found which, together with the pressure will give the amount not adsorbed. The difference between this amount and the amount of gas admitted was considered to be the amount adsorbed.

In all measurements given below, the volumes of gas are reduced to standard temperature and pressure.

1. TIME REQUIRED FOR EQUILIBRIUM

In order to obtain some idea as to the time required for equilibrium between the adsorbed and unadsorbed gas to be attained, a measured amount of dry air was admitted to the apparatus and al-

lowed to be in contact with the lignite which was kept at a constant temperature (20°C.).

The pressure readings given by the manometer, L, were taken at intervals for the three succeeding days. The amount adsorbed was calculated, the results being given in Table I.

TABLE I

	Amount admitted	Time (t)	Pressure	Amount adsorbed (x)	t/x
1.....	161.4 cc.	0.0 hrs.	344.0 mm.	24.8 cc.	0
2.....		.05	312.5	37.4	.0014
3.....		.25	294.0	44.8	.0056
4.....		.5	288.2	47.0	.011
5.....		1.0	284.0	48.7	.021
6.....		2.0	280.0	50.3	.039
7.....		5.0	275.5	52.1	.096
8.....		7.0	273.0	52.9	.132
9.....		10.0	269.5	54.5	.183
10.....		12.0	268.0	55.0	.218
11.....		15.0	265.5	56.3	.266
12.....		20.0	262.2	57.3	.349
13.....		25.0	258.0	59.1	.423
14.....		30.0	255.0	60.2	.498
15.....		35.0	254.5	60.5	.578
16.....		40.0	253.5	60.8	.658
17.....		50.0	252.0	61.5	.813
18.....		60.0	251.5	61.6	.974

The curves for the relation between the amount adsorbed (x) and the time (t) are shown in Fig. 2. The part of the curve between A and B shows that at first the adsorption takes place very quickly and represents the condensation of the gas upon the surface of the lignite. The other part, between B and C represents the slower diffusion into the interior of the lignite. Thus the process is much the same as for coconut charcoal.

The curve plotted between t and t/x approximates a straight line showing that the equation for the curve for x and t is of the form:

$$t/x = a + bt$$

where a and b are constants.

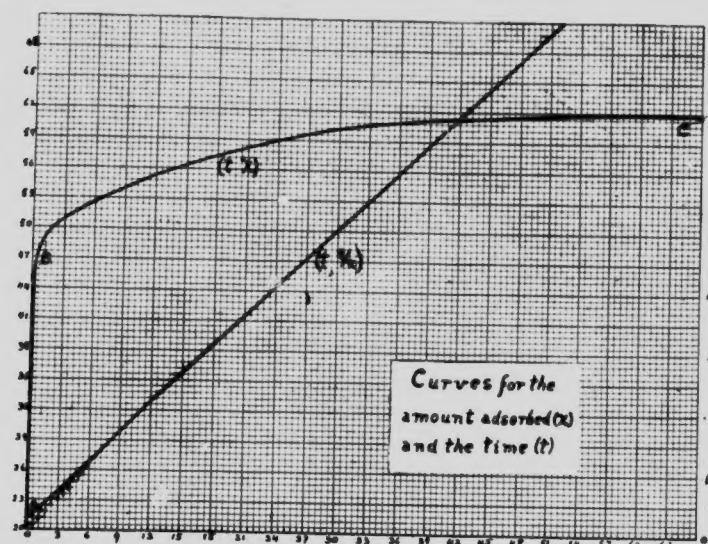


Figure 2

2. INFLUENCE OF TEMPERATURES ON THE ADSORPTION OF GASES

Experiments on the adsorption of air were carried out at three temperatures: 20°C., -78°C. and -190°C. The first temperature was obtained by immersing the lignite tube in a water bath contained in a liquid air flask and kept constant at 20°C.; the second, by using a mixture of solid carbon dioxide and ether, the carbon dioxide being added at intervals to keep it at the same temperature, and the third, by using liquid air. Before it was admitted to the apparatus, the air was carefully dried by phosphorous pentoxide.

The following table gives the results of the experiment with the lignite at 20°C.:

TABLE II

Amount admitted	Time for saturation	Amount adsorbed (x)	Log x	Pressure (p)	Log p.
76.8 cc.	50 hours	29.5 cc.	1.470	119 mm.	2.076
156.8		60.4	1.781	243.0	2.386
236.6		89.6	1.952	370.5	2.569
279.0		106.4	2.027	435.0	2.639
321.9		122.7	2.089	502.0	2.701
363.2		137.1	2.137	570.0	2.756
397.9		147.9	2.170	630.0	2.799

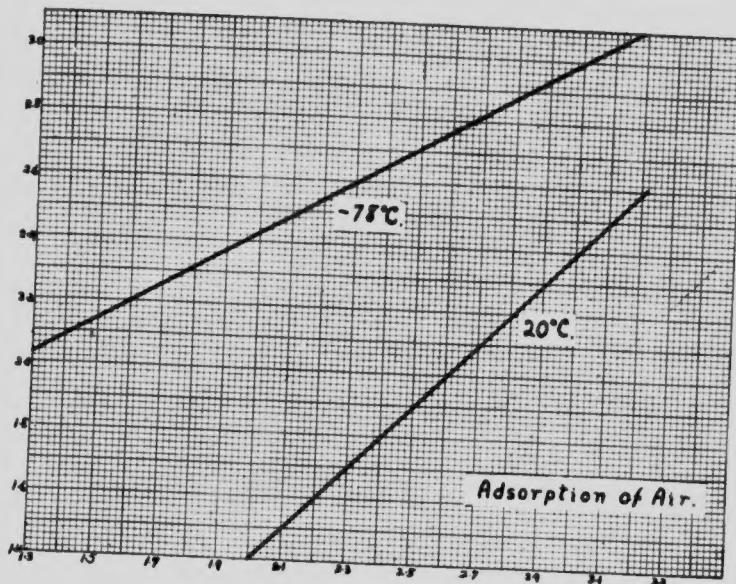


Figure 3

If $\log x$ be plotted against $\log p$, the curve obtained is a straight line (see Fig. 3), which shows that the equation giving the relation between the amount and the pressure is of the form:

$$x = ap^b$$

where a and b are constants. Substituting the above results in this equation, it becomes:

$$x = .43p^{.9}$$

When the temperature of the lignite was much below the temperature of the room, a correction had to be made for the fall of pressure in the apparatus due to the cooling of the lignite tube. The amount of this correction was determined experimentally. The lignite was removed and the tube filled with an equal volume of a non-absorbing material (copper). The cooling agent was then applied and the fall of pressure noted. A series of readings showed that the fall of pressure is proportional to the initial pressure. This correction has been applied to all the pressure readings given for the other two temperatures.

The following results were obtained with the lignite at $-78^\circ\text{C}.$:

TABLE III

Amount admitted	Limit for saturation	Amount adsorbed	Log. x	Press. p	Log. p
126.5	36 hours	116.3 cc.	2.066	234 mm.	1.369
541.1		450.4	2.654	207.1	2.316
826.4		645.3	2.810	413.8	2.617

The equation for x and p for this temperature is of the same form as before (see Fig. 3)

$$x = 17 \cdot 7 p^{86}$$

One reading was made with the lignite at liquid air temperature:

TABLE IV

Amount admitted	Time for saturation	Amount adsorbed	Log. x	Press.	Log. p.
939.6 cc.	60 hours	888.0 cc.	2.948	81.6 mm.	1.912

THE ADSORPTION OF CARBON DIOXIDE

An experiment on the adsorption of carbon dioxide was made with the lignite at 20°C. The gas used was that which is manufactured commercially and it was dried by bubbling it through strong sulphuric acid before it was put into the apparatus.

The following results show that carbon dioxide is adsorbed much more readily than air:

TABLE V

Amount admitted	Time for saturation	Amount adsorbed (x)	Log x	Pressure (p.)	Log p.
420.6 cc.	10 hours	375.2 cc.	2.574	114 mm.	2.057
631.4		537.2	2.730	237.0	2.375
758.8		626.7	2.797	332.0	2.521
886.9		711.7	2.852	438.5	2.642
1051.1		810.4	2.909	602.5	2.780

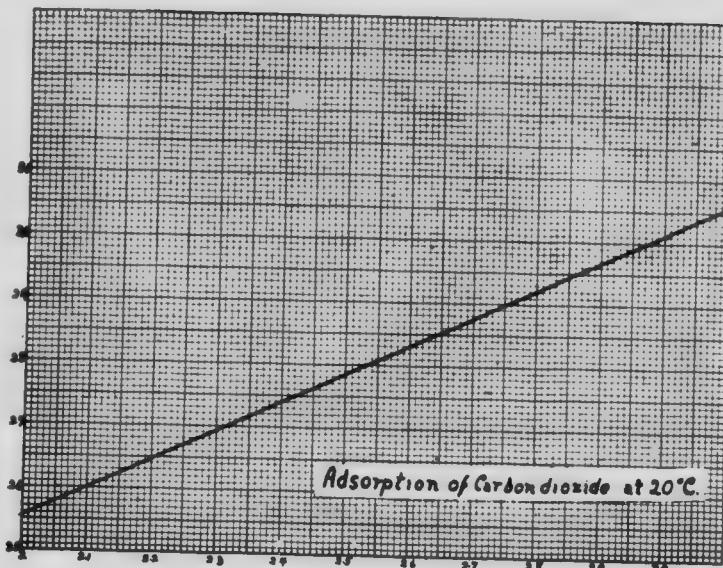


Figure 4

The adsorption-pressure equation for carbon dioxide with the lignite at 20°C. was found to be: (see Fig. 4).

$$x = 42.7 p^{.46}$$

THE ADSORPTION OF HYDROGEN

With the lignite at 20°C., very little hydrogen is adsorbed. The following results were obtained but they do not conform to those obtained for other gases:

TABLE VI

Amount admitted	Amount adsorbed (x)	Log x	Pressure (p)	Log p.
99.4 cc.	2.8 cc.	.447	243 mm.	2.386
141.1	5.2	.716	342	2.534
182.4	7.4	.869	440	2.644
224.6	13.6	1.134	535	2.728

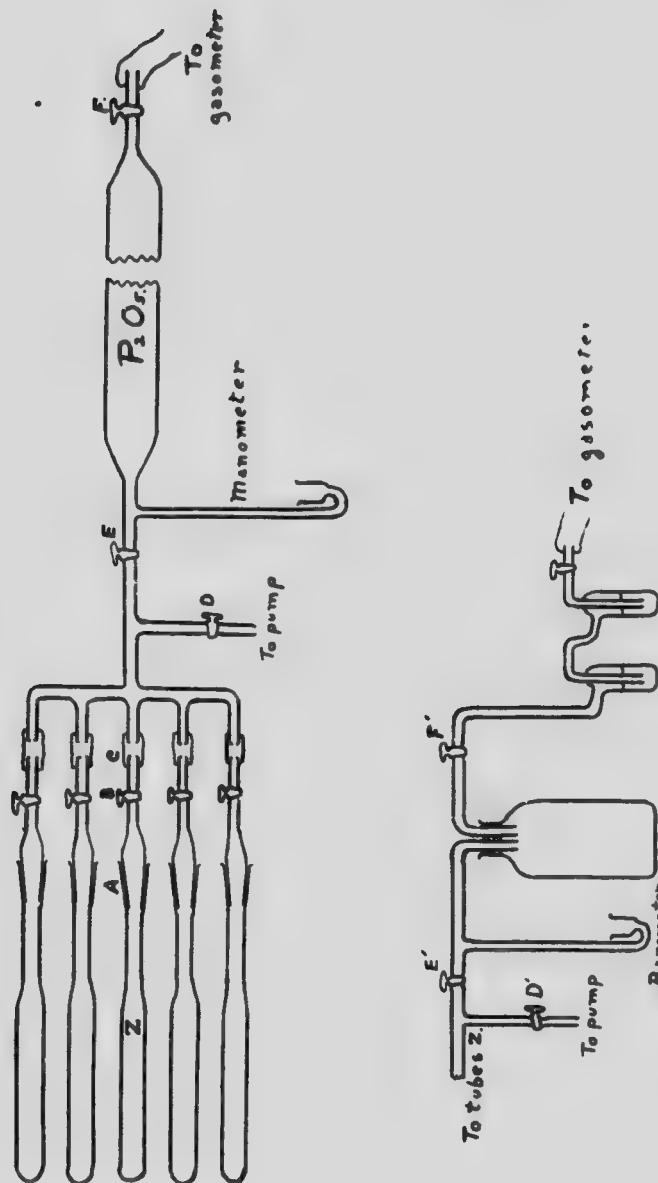


Figure 5

3. TEST OF POSSIBLE CHEMICAL COMBINATION OF LIGNITE AND GASES

To find out whether any chemical action or permanent adsorption takes place, the apparatus shown in Fig. 5 was set up. Five samples of lignite carbonised at different temperatures were put in the tubes at Z. These samples were: raw lignite and lignite carbonised at 105°C., 350°C., 450°C. and 550°C. They had not been exposed to the air since carbonisation except where they were transferred to these tubes and then they were immediately heated to their respective temperatures and each tube exhausted.

The weight of each tube was found and the lignite exposed to the gas for a time sufficient for saturation to take place. The tubes were then weighed, heated out, exhausted and weighed again. If the last weight was appreciably different from the first, then chemical action or permanent adsorption must be taking place.

Readings were made for three gases: dry nitrogen, dry oxygen and moist oxygen. The results are given in Tables VII, VIII and IX. In the first column is given the temperature at which the lignite was carbonised; column 2 gives the net weight of the lignite and column 3 the weight after the lignite was saturated with the gas at atmospheric pressure, the difference denoting the gas absorbed is given in the next column. Column 5 repeats column 2, and column 6 gives the final net weight of the lignite after it had been heated and exhausted. The last column gives the difference between the initial and final weights of the samples, and consequently shows the net gain or loss in weight during the whole operation.

TABLE VII

Dry Nitrogen

Sample	First Weight	Second Weight	Difference	First Weight	Last Weight	Difference
Raw	58.7174	58.7090	.3196	58.7174	58.3904	-.3270
105°C	57.5468	57.5872	.0404	57.5468	57.5486	+.0018
350°C	51.6405	51.6832	.0246	51.6406	51.6360	-.0046
450°C	47.9974	48.0266	.0294	47.9974	48.0042	+.0078
550°C	43.6116	43.6276	.0160	43.6116	43.5985	-.0131

TABLE VIII

Dry Oxygen

Sample	First Weight	Second Weight	Difference	First Weight	Last Weight	Difference
Raw	58.3904	58.4095	.0181	58.3904	57.9922	+.3982
"	57.9976	58.0158	.0182	57.9976	57.9474	-.0502
105°C	57.5486	57.6048	.0562	57.5486	57.5572	+.0086
"	57.5580	57.6100	.0520	57.5580	57.5594	+.0014
350°C	51.6360	51.7812	.1452	51.6360	51.6336	-.0024
"	51.7546	51.9074	.1528	51.7546	51.7158	-.0388
450°C	48.0042	48.1636	.1594	48.0042	47.9964	-.0074
"	47.2041	47.4244	.2203	47.2041	47.1508	-.0533
550°C	43.5985	43.7154	.1169	43.5985	43.5732	-.0253
"	42.5328	42.6366	.1038	42.5328	42.4222	-.1106

TABLE IX

Moist Oxygen

Sample	First Weight	Second Weight	Difference	First Weight	Last Weight	Difference
Raw	57.9474	57.9681	.0207	57.9474	57.9025	-.0451
105°C	57.5594	57.6126	.0532	57.5594	57.5670	+.0076
350°C	51.7158	51.8690	.1532	51.7158	51.7098	-.0060
450°C	47.1508	47.3561	.2053	47.1508	47.1156	-.0342
550°C	42.4222	42.5870	.1648	42.4222	42.4238	+.0016

From the above tables, the following conclusions may be drawn:

1. Oxygen is adsorbed much more readily than nitrogen.
2. The presence of water vapour decreases the amount of gas adsorbed. This is shown from the last two tables. The weight of the amount adsorbed is not increased and the weight includes that of the water vapour taken up by the samples.
3. No permanent adsorption takes place since there are but few cases where the last weight is greater than the first, and these may be due to experimental error.
4. Chemical action may be taking place in the case of oxygen. The fact that in most cases the last weight is less than the first indicates that the oxygen combines with the lignite forming carbon dioxide, which is given off when the lignite is heated, making the sample lighter.

This work was done under the direction of Professor E. F. Burton.

UNIVERSITY OF TORONTO STUDIES

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